[0051]   Of the above groups, alkyl-substituted cyclopentadienyl groups are particularly preferable.

[0052]   When the compound represented by the formula (i) contains as the ligands L two or more groups having cyclopentadienyl skeleton. two of them may be bonded through an alkylene group such as ethylene or propylene. a substituted alkylene group such as isopropylidene or diphenylmethylene. a silylene group, or a substituted silylene group such as dimethylsilylene. diphenylsilylene or methylphenylsilylene.

[0053]   The ligand L other than the ligand having cyclopentadienyl skeleton is, for example, a hydrocarbon group of 1 to 12 carbon atoms, an alkoxy group, an aryloxy group, a sulfonic acid-containing group ($-SO_3R^a$ wherein R^a is an alkyl group, a halogen-substituted alkyl group, an aryl group, a halogen-substituted aryl group or an alkyl-substituted aryl group), a halogen atom or a hydrogen atom.

[0054]   Examples of the hydrocarbon groups of 1 to 12 carbon atoms include alkyl groups, cycloalkyl groups, aryl groups and aralkyl groups. More specifically, there can be mentioned:

alkyl groups, such as methyl, ethyl, n-propyl. isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, pentyl, hexyl, octyl, decyl and dodecyl;
cycloalkyl groups, such as cyclopentyl and cyclohexyl;
aryl groups, such as phenyl and tolyl; and
aralkyl groups, such as benzyl and neophyl.

[0055]   Examples of the alkoxy groups include methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy, t-butoxy, pentoxy, hexoxy and octoxy.

[0056]   An example of the aryloxy group is phenoxy.

[0057]   Examples of the sulfonic acid-containing groups ($-SO_3R^a$) include methanesulfonato, p-toluenesulfonato, tri-fluoromethanesulfonato and p-chlorobenzenesulfonato.

[0058]   The halogen atom is fluorine, chlorine, bromine or iodine.

[0059]   Examples of the metallocene compounds having zirconium as M and containing at least two ligands having cyclopentadienyl skeleton include:

bis(methylcyclopentadienyl)zirconium dichloride,
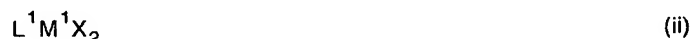bis(ethylcyclopentadienyl)zirconium dichloride,
bis(n-propylcyclopentadienyl)zirconium dichloride,
bis(indenyl)zirconium dichloride, and
bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride.

[0060]   Compounds wherein the zirconium metal is replaced with a titanium metal or a hafnium metal in the above compounds are also employable.

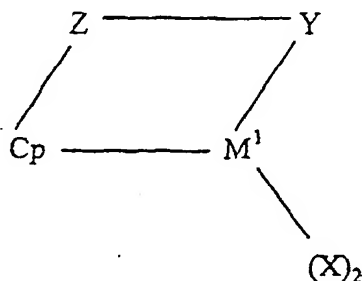[0061]   Also employable as the metallocene compound is a compound represented by the following formula (ii):

$$L^1M^1X_2 \tag{ii}$$

wherein M is a metal of Group 4 of the periodic table or a metal of lanthanide series,

L^1 is a derivative of a delocalized π-bonding group and imparts a restraint geometric shape to the active site of the metal M^1, and
each X is independently hydrogen, halogen, a hydrocarbon group containing 20 or less carbon atoms, a silyl group containing 20 or less silicon atoms, or a germyl group containing 20 or less germanium atoms.

[0062]   Of the compounds represented by the formula (ii), a compound represented by the following formula (iii) is preferable.

$$Z \longrightarrow Y$$

(formula iii)

Cp ———— M¹

$(X)_2$

(iii)

[0063]   In the above formula, M^1 is titanium, zirconium or hafnium, and X is the same as above.

[0064]   Cp is a substituted cyclopentadienyl group π-bonded to M^1 and having a substituent group Z.

[0065]   Z is oxygen, sulfur, boron or an element of Group 14 of the periodic table (e.g., silicon, germanium or tin).

[0066]   Y is a ligand containing nitrogen, phosphorus, oxygen or sulfur.

[0067]   Z and Y may together form a condensed ring.

[0068]   Examples of the metallocene compounds represented by the formula (iii) include:

(dimethyl(t-butylamido)(tetramethyl-η^5-cyclopentadienyl)silane)titanium dichloride,
((t-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyl)titanium dichloride,
(dibenzyl(t-butylamido)(tetramethyl-η^5-cyclopentadienyl)silane)titanium dichloride,
(dimethyl(t-butylamido)(tetramethyl-η^5-cyclopentadienyl)silane)dibenzyltitanium,
(dimethyl(t-butylamido)(tetramethyl-η^5-cyclopentadienyl)silane)dimethyltitanium,
((t-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyl)dibenzyltitanium,
((methylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyl)dineopentyltitanium,
((phenylphosphido)(tetramethyl-η^5-cyclopentadienyl)methylene)diphenyltitanium,
(dibenzyl (t-butylamido) (tetramethyl-η^5-cyclopentadienyl)silane)dibenzyltitanium,
(dimethyl (benzylamido) (η^5-cyclopentadienyl) silane) di (trimethylsilyl) titanium,
(dimethyl(phenylphosphido)(tetramethyl-η^5-cyclopentadienyl)silane)dibenzyltitanium,
((tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyl)dibenzyltitanium,
(2-η^5-(tetramethyl-cyclopentadienyl)-1-methyl-ethanolate(2-))dibenzyltitanium,
(2-η^5-(tetramethyl-cyclopentadienyl)-1-methyl-ethanolate(2-))dimethyltitanium,
(2-((4a, 4b, 8a, 9, 9a-η)-9H-fluorene-9-yl)cyclohexanolate(2-))dimethyltitanium, and
(2-((4a,4b,8a,9,9a-η)-9H-fluorene-9-yl)cyclohexanolate(2-))dibenzyltitanium.
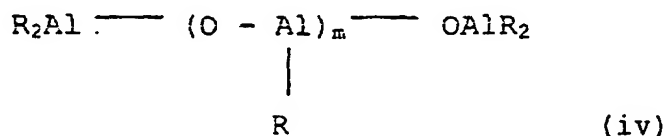
[0069]   Compounds wherein the titanium metal is replaced with a zirconium metal or a hafnium metal in the above compounds are also employable.
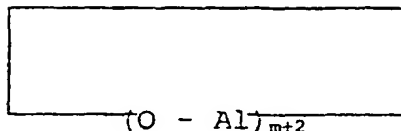
[0070]   The metallocene compounds mentioned above can be used singly or in combination of two or more kinds.

[0071]   In the present invention, a zirconocene compound having zirconium as the central metal atom and containing at least two ligands having cyclopentadienyl skeleton is preferably used as the metallocene compound represented by the formula (i). As the metallocene compound represented by the formula (ii) or (iii), a compound having titanium as the central metal atom is preferable. Of the metallocene compounds mentioned above, a compound represented by the formula (iii) and having titanium as the central metal atom is particularly preferable.

[0072]   The organoaluminum oxy-compound for forming the metallocene catalyst may be aluminoxane hitherto known or a benzene-insoluble organoaluminum oxy-compound.

[0073]   The hitherto known aluminoxane is represented by the following formula:

$$R_2Al \overline{} (O - Al)_m \overline{} OAlR_2$$
$$|$$
$$R$$

(iv)

$$(O - Al)_{m+2}$$

(v)

In the formulas (iv) and (v), R is a hydrocarbon group, such as methyl, ethyl, propyl or butyl, preferably methyl or ethyl, particularly preferably methyl; and m is an integer of 2 or more, preferably an integer of 5 to 40.

[0074]   The aluminoxane may be composed of mixed alkyloxyaluminum units consisting of alkyloxyaluminum units represented by the formula $OAl(R^1)$ and alkyloxyaluminum units represented by the formula $OAl(R^2)$ (each of R^1 and R^2 is the same hydrocarbon group as indicated by R, and R^1 and R^2 are groups different from each other).

[0075]   Examples of the ionizing ionic compounds for forming the metallocene catalyst include Lewis acid and an ionic compound.

[0076]   The Lewis acid is, for example, a compound represented by BR_3 (R is a phenyl group which may have a substituent group such as fluorine, methyl or trifluoromethyl, or fluorine). Examples of such compounds include trifluoroboron, triphenylboron, tris(4-fluorophenyl)boron, tris(3,5-difluorophenyl)boron, tris(4-fluoromethylphenyl)boron, tris(pentafluorophenyl)boron, tris(p-tolyl)boron, tris(o-tolyl)boron and tris(3,5-dimethylphenyl)boron.

[0077]   The ionic compound is, for example, a trialkyl-substituted ammonium salt, an N,N-dialkylanilinium salt, a dialkylammonium salt or a triarylphosphonium salt.

[0078]   Examples of the trialkyl-substituted ammonium salts include:

triethylammoniumtetra(phenyl)boron,
tripropylammoniumtetra(phenyl)boron,
tri(n-butyl)ammoniumtetra(phenyl)boron,
trimethylammoniumtetra(p-tolyl)boron,
trimethylammoniumtetra(o-tolyl)boron,
tributylammoniumtetra(pentafluorophenyl)boron,
tripropylammoniumtetra(o,p-dimethylphenyl)boron,
tributylammoniumtetra(m,m-dimethylphenyl)boron,
tributylammoniumtetra(p-trifluoromethylphenyl)boron, and
tri(n-butyl)ammoniumtetra(o-tolyl)boron.

[0079]   Examples of the N,N-dialkylanilinium salts include:

N,N-dimethylaniliniumtetra(phenyl)boron,
N,N-diethylaniliniumtetra(phenyl)boron, and
N,N-2,4,6-pentamethylaniliniumtetra(phenyl)boron.

[0080]   Examples of the dialkylammonium salts include:

di(1-propyl)ammoniumtetra(pentafluorophenyl)boron, and
dicyclohexylammoniumtetra(phenyl)boron.

[0081]   Also employable as the ionic compound is triphenylcarbeniumtetrakis(pentafluorophenyl)borate, N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate or ferroceniumtetra(pentafluorophenyl)borate. In particular, the ionizing ionic compound is preferably used because it controls composition distribution of the ethylene/α-olefin copolymer.

[0082]   For forming the metallocene catalyst, an organoaluminum compound may be used together with the organoaluminum oxy-compound and/or the ionizing ionic compound.

[0083]   The organoaluminum compound is, for example, a compound represented by the following formula (vi):

$$R^1_n AlX_{3-n}$$

(vi)

wherein R^1 is a hydrocarbon group of 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms, X is a halogen atom or a

hydrogen atom. and n is 1 to 3.

[0084] The hydrocarbon group of 1 to 15 carbon atoms is. for example, an alkyl group, a cycloalkyl group or an aryl group. Examples of such groups include methyl. ethyl. n-propyl. isopropyl. isobutyl. pentyl. hexyl, octyl, cyclopentyl. cyclohexyl, phenyl and tolyl.

[0085] Examples of the organoaluminum compounds include:

trialkylaluminums, such as trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum. trioctylaluminum and tri-2-ethylhexylaluminum;

alkenylaluminums represented by the formula $(i\text{-}C_4H_9)_x Al_y (C_5H_{10})_z$ (wherein x, y and z are each a positive number, and $z \geq 2x$), such as isoprenylaluminum;

trialkenylaluminums, such as triisopropenylaluminum;

dialkylaluminum halides, such as dimethylaluminum chloride, diethylaluminum chloride, diisopropylaluminum chloride, diisobutylaluminum chloride and dimethylaluminum bromide;

alkylaluminum sesquihalides, such as methylaluminum sesquichloride, ethylaluminum sesquichloride, isopropylaluminum sesquichloride, butylaluminum sesquichloride and ethylaluminum sesquibromide,

alkylaluminum dihalides, such as methylaluminum dichloride, ethylaluminum dichloride, isopropylaluminum dichloride and ethylaluminum dibromide;

dialkylaluminum hydrides, such as diethylaluminum hydride and dibutylaluminum hydride; and

alkylaluminum dihydrides, such as ethylaluminum dihydride and propylaluminum dihydride.

[0086] In the present invention, ethylene, an α-olefin of 3 to 20 carbon atoms, and if necessary, other monomers are copolymerized in the presence of the metallocene catalyst, usually in a liquid phase. In the copolymerization, a hydrocarbon solvent is generally used as a polymerization solvent, but an α-olefin such as propylene may be used as the solvent.

[0087] Examples of the hydrocarbon solvents used in the polymerization include aliphatic hydrocarbons, such as pentane, hexane, heptane, octane, decane, dodecane and kerosine, and halogen derivatives thereof; alicyclic hydrocarbons, such as cyclohexane, methylcyclopentane and methylcyclohexane, and halogen derivatives thereof; and aromatic hydrocarbons, such as benzene, toluene and xylene, and halogen derivatives thereof such as chlorobenzene. These solvents can be used singly or in combination of two or more kinds.

[0088] Although ethylene, an α-olefin of 3 to 20 carbon atoms, and if necessary, other monomers can be copolymerized by any of batchwise and continuous processes, the copolymerization is preferably carried out continuously, and is particularly preferably carried out continuously using a stirring vessel type reactor. When the copolymerization is carried out continuously, the metallocene catalyst is used in, for example, the following concentration.

[0089] The concentration of the metallocene compound in the polymerization system is in the range of usually 0.00005 to 0.1 mmol/liter (polymerization volume), preferably 0.0001 to 0.05 mmol/liter. The organoaluminum oxy-compound is fed in such an amount that the molar ratio (Al/transition metal) of the aluminum atom to the transition metal in the metallocene compound in the polymerization system becomes usually 1 to 10000, preferably 10 to 5000.

[0090] The ionizing ionic compound is fed in such an amount that the molar ratio (ionizing ionic compound/metallocene compound) of the ionizing ionic compound to the metallocene compound in the polymerization system becomes 0.5 to 30, preferably 1 to 25.

[0091] When the organoaluminum compound is used, the compound is fed in an amount of usually about 0 to 5 mmol/liter (polymerization volume), preferably about 0 to 2 mmol/liter.

[0092] In the copolymerization of ethylene, an α-olefin of 3 to 20 carbon atoms, and if necessary, other monomers in the presence of the metallocene catalyst, the copolymerization reaction is carried out under the conditions of a temperature of usually -20 to 150°C, preferably 0 to 120°C, more preferably 0 to 100°C, and a pressure of more than 0 kg/cm² and not more than 80 kg/cm², preferably more than 0 kg/cm² and not more than 50 kg/cm². In a continuous polymerization process, these polymerization conditions are preferably held constant.

[0093] Although the reaction time (average residence time when the copolymerization is carried out continuously) varies depending upon the catalyst concentration, polymerization temperature, etc., it is in the range of usually 5 minutes to 5 hours, preferably 10 minutes to 3 hours.

[0094] Ethylene, an α-olefin of 3 to 20 carbon atoms, and if necessary, other monomers are fed to the polymerization system in such amounts that the ethylene/α-olefin copolymer having specific composition can be obtained. In the copolymerization, a molecular weight modifier such as hydrogen may be further used.

[0095] When ethylene, an α-olefin of 3 to 20 carbon atoms, and if necessary, other monomers are copolymerized as described above, the ethylene/α-olefin copolymer is usually obtained as a polymer solution containing the copolymer. The polymer solution is treated in a conventional manner, whereby the ethylene/α-olefin copolymer for use in the invention is obtained.

Lubricating oil composition

[0096] The lubricating oil composition according to the invention is a lubricating oil composition comprising a lubricating oil base (A) and the above-mentioned ethylene/α-olefin copolymer (B), or a lubricating oil composition comprising a lubricating oil base (A), the specific ethylene/α-olefin copolymer (B) and a pour point depressant (C).

[0097] The components for forming the lubricating oil composition of the invention are described below.

(A) Lubricating oil base

[0098] Examples of the lubricating oil bases (A) for use in the invention include mineral oils and synthetic oils such as poly-α-olefins, polyol esters, diesters (e.g., dioctyl phthalate, dioctyl sebacate) and polyalkylene glycols. A mineral oil or a blend of a mineral oil and a synthetic oil is preferably employed. The mineral oil is generally employed after subjected to refining such as dewaxing. Although mineral oils are divided into several classes according to the refining method, a mineral oil having a wax content of 0.5 to 10 % is generally employed. For example, a highly refined oil produced by hydrocracking refining, having a low pour point and a high viscosity index and containing isoparaffin as a main component is employable. A mineral oil having a kinematic viscosity of 10 to 200 cSt at 40°C is generally employed.

(B) Ethylene/α-olefin copolymer

[0099] As the ethylene/α-olefin copolymer (B) for use in the present invention, the aforesaid ethylene/α-olefin copolymer is employed.

[0100] In the lubricating oil composition of the invention, particularly an ethylene/α-olefin copolymer (B-1) having the following properties is preferably employed as the ethylene/α-olefin copolymer (B);

(1) the ethylene content (E) is in the range of 65 to 77 % by weight,
(2) the weight-average molecular weight (Mw) in terms of polystyrene, as measured by GPC, is in the range of 80,000 to 400,000,
(3) Mw/Mn is not more than 2.4,
(4) the melting point (Tm) as measured by DSC is in the range of 15 to 60°C,
(5) the ethylene content (E, % by weight) and the melting point (Tm, °C) as measured by DSC satisfy the following relation (I):

$$3.31 \times E\text{-}186 \geq Tm \tag{I},$$

and
(6) the proportion (V, %) of αβ carbon atoms to all carbon atoms in the main chain, and if present, the long-chain branches, and the ethylene content (E, % by weight) satisfy the following relation (II):

$$V \leq 10\text{-}0.1 \times E \tag{II}.$$

[0101] Further, an ethylene/α-olefin copolymer (B-2) having the following properties can be also preferably employed as the ethylene/α-olefin copolymer (B) ;

(1) the ethylene content (E) is in the range of 40 to 55 % by weight,
(2) the weight-average molecular weight (Mw) in terms of polystyrene, as measured by GPC, is in the range of 80,000 to 400,000,
(3) Mw/Mn is not more than 2.4,
(4) the melting point (Tm) as measured by DSC is not higher than -20°C,
(5) the ethylene content (E, % by weight) and the melting point (Tm, °C) as measured by DSC satisfy the following relation (I):

$$3.31 \times E\text{-}186 \geq Tm \tag{I},$$

and

(6) the proportion (V. %) of $\alpha\beta$ carbon atoms to all carbon atoms in the main chain. and if present. the long-chain branches. and the ethylene content (E, % by weight) satisfy the following relation:

$$V \leq 10\text{-}0.1 \times E \qquad\qquad (II).$$

[0102]   The ethylene/α-olefin copolymer (B) is preferably a copolymer having a ratio (I_{10}/I_2) of the melt index (I_{10}) as measured at 190°C under a load of 10 kg to the melt index (I_2) as measured at 190°C under a load of 2.16 kg ranging from 8 to 16.

[0103]   Further, the ethylene/α-olefin copolymer (B) is preferably a copolymer having a ratio (I_{10}/I_2) of the melt index (I_{10}) as measured at 190°C under a load of 10 kg to the melt index (I_2) as measured at 190°C under a load of 2.16 kg being not less than 5 and less than 8.

(C) Pour point depressant

[0104]   Examples of the pour point depressants for use in the invention include alkylated naphthalene, (co)polymers of alkyl methacrylates, (co)polymers of alkyl acrylates, copolymers of alkyl fumarates and vinyl acetate, α-olefin polymers, and copolymers of α-olefins and styrene. Of these, (co)polymers of alkyl methacrylates and (co)polymers of alkyl acrylates are preferably employed.

Lubricating oil composition

[0105]   The first embodiment of the lubricating oil composition of the invention comprises the lubricating oil base (A) and the ethylene/α-olefin copolymer (B). In this lubricating oil composition, the ethylene/α-olefin copolymer (B) is contained in an amount of 1 to 20 % by weight, preferably 5 to 10 % by weight (residue: lubricating oil base (A) and additives described later).

[0106]   Such a lubricating oil composition exhibits small temperature dependence and has excellent low-temperature properties. The lubricating oil composition can be used as it is as a lubricating oil, or can be used as a lubricating oil after further blended with a lubricating oil base, a pour depressant, etc.

[0107]   The second embodiment of the lubricating oil composition of the invention comprises the lubricating oil base (A), the ethylene/α-olefin copolymer (B) and the pour point depressant (C). In this lubricating oil composition, the ethylene/α-olefin copolymer (B) is contained in an amount of 0.1 to 5 % by weight, preferably 0.2 to 1.5 % by weight, more preferably 0.25 to 1.5 % by weight, particularly preferably 0.30 to 1.5 % by weight, and the pour point depressant (C) is contained in an amount of 0.05 to 5 % by weight, preferably 0.1 to 3 % by weight, more preferably 0.1 to 2 % by weight, most preferably 0.2 to 1.5 % by weight, (residue: lubricating oil base (A) and additives described later). When the amount of the ethylene/α-olefin copolymer (B) in the lubricating oil composition of the invention is not less than 0.1 % by weight, a viscosity improving effect can be obtained, and when the amount thereof is not more than 5 % by weight, the effect of the pour point depressant (C) is not hindered, so that the above range is preferable. When the amount of the ethylene/α-olefin copolymer (B) is in the above range, a lubricating oil composition having improved viscosity and excellent flowability at low temperatures can be obtained.

[0108]   Such a lubricating oil composition exhibits small temperature dependence and small rise of the pour point, said rise being attributed to the interaction between the ethylene/α-olefin copolymer and the pour point depressant, and has excellent low-temperature properties in every shear rate region. Moreover, the lubricating oil composition has excellent high-temperature properties and shows good lubricity, so that it is advantageous in saving of fuel.

[0109]   In the lubricating oil composition of the invention, additives exhibiting viscosity index improving effect, such as (co)polymers of alkyl methacrylates, hydrogenated SBR or SEBS, and other additives, such as detergent, rust preventive agent, dispersant, extreme pressure agent, anti-foaming agent, antioxidant and metal deactivator, may be contained in addition to the lubricating oil base. (A), the ethylene/α-olefin copolymer (B) and the pour point depressant (C).

[0110]   The lubricating oil composition of the invention can be prepared in the following manner: the ethylene/α-olefin copolymer (B), and if necessary, additives are mixed with or dissolved in the lubricating oil base (A) in accordance with a known method; or the ethylene/α-olefin copolymer (B), the pour point depressant (C), and if necessary, additives are mixed with or dissolved in the lubricating oil base (A) in accordance with a known method.

[0111]   In the present specification, all numerical values for the amounts of materials, reaction conditions, molecular weights, carbon atom numbers, etc. are desirably understood to be supplemented with a term "about" so long as their meanings do not become technically indefinite, with the exception of the following examples or unless otherwise stated.

EFFECT OF THE INVENTION

[0112]   The lubricating oil composition of the invention is excellent in the low-temperature properties and the lubricity at high temperatures.

EXAMPLE

[0113]   The present invention is further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

[0114]   In the examples, various properties were measured in the following manner.

Ethylene content (E)

[0115]   The ethylene content was measured in a mixed solvent of orthodichlorobenzene and benzene-d6 (orthod-ichlorobenzene/benzene-d6 = 3/1 - 4/1, by volume) using a nuclear magnetic resonance apparatus of Japan Electron Optics Laboratory LA500 Model under the conditions of a temperature of 120°C, a pulse width of 45° pulse and a pulse repetition time of 5.5 seconds.

Viscosity at 100°C (K.V.)

[0116]   The viscosity was measured in accordance with ASTM D 445. In the examples, adjustment was made so as to obtain K.V. of about 10 mm^2/sec.

Cold Cranking Simulator (CCS)

[0117]   CCS was measured in accordance with ASTM D 2602. The CCS is used to evaluate sliding properties (starting properties) at low temperatures at the crank shaft. A smaller value of CCS indicates better low-temperature properties of a lubricating oil.

Mini-Rotary Viscometer (MRV)

[0118]   MRV was measured in accordance with ASTM D 3829 and D 4684. The MRV is used to evaluate pumping performance of an oil pump at low temperatures. A smaller value of MRV indicates better low-temperature properties of a lubricating oil.

Shear Stability Index (SSI)

[0119]   SSI was measured in accordance with ASTM D 3945. The SSI is a measure of kinematic viscosity loss that is caused by break of molecular chain of a copolymer component in a lubricating oil when the copolymer component suffers a shear force under the sliding motion. A larger value of SSI indicates larger loss of kinematic viscosity.

High Temperature High Shear Viscosity (HTHS)

[0120]   HTHS was measured under the conditions of $150°C/10^6 s^{-1}$ in accordance with ASTM D 4624. The HTHS is used to evaluate lubricating oil performance at high temperatures at a high shear rate. A larger value of HTHS indicates better lubricating oil performance at high temperatures.

Low-temperature storage stability

[0121]   After a lubricating oil was cooled at -18°C for 2 weeks, flowability (appearance) of the lubricating oil was observed and evaluated as follows.

AA: The lubricating oil flows.
BB: The lubricating oil does not flow (in gel state).

Polymerization Example 1

Synthesis of olefin copolymer

[0122] In a 2-liter autoclave (made of SUS) equipped with a stirring blade, said autoclave having been thoroughly purged with nitrogen, 900 ml of heptane was placed at 23°C. To the autoclave, 5 Nl of propylene and 90 ml of hydrogen were fed while rotating the stirring blade and ice cooling. Then, the autoclave was heated up to 70°C and pressurized with ethylene so that the total pressure would become 6 KG. When the internal pressure of the autoclave became 6 KG, 1.0 ml of a hexane solution of triisobutylaluminum (TIBA) (1.0 mM/ml) was forced into the autoclave with nitrogen. Subsequently, 3 ml of the previously prepared toluene solution containing 0.016 mM (in terms of B) of triphenylcarbe-nium(tetrakispentafluorophenyl)borate and 0.0004 mM of (dimethyl(t-butylamido)(tetramethyl-η^5-cyclopentadienyl)si-lane)titanium dichloride was forced into the autoclave with nitrogen to initiate polymerization. Thereafter, for a period of 5 minutes, temperature control of the autoclave was made so that the internal temperature would become 70°C, and ethylene was directly fed so that the pressure would become 6 KG. After 5 minutes from the initiation of polymer-ization, to the autoclave was fed 5 ml of methanol by means of a pump to terminate polymerization, and the pressure of the autoclave was released to atmospheric pressure. Then, 3 liters of methanol was poured into the reaction solution with stirring. The resulting polymer with the solvent was dried at 130°C and 600 Torr for 13 hours to obtain 32 g of an ethylene/propylene copolymer. Properties of the resulting polymer are set forth in Table 1.

Polymerization Example 2

[0123] 35 Grams of a polymer was obtained in the same manner as in Example 1, except that the charge of propylene was changed to 4.5 Nl. Properties of the resulting polymer are set forth in Table 1.

Polymerization Example 3

[0124] 38 Grams of a polymer was obtained in the same manner as in Example 1, except that the charge of hydrogen was changed to 150 ml and the polymerization time was changed to 4 minutes. Properties of the resulting polymer are set forth in Table 1.

Polymerization Example 4

[0125] In a 2-liter autoclave (made of SUS) equipped with a stirring blade, said autoclave having been thoroughly purged with nitrogen, 900 ml of heptane was placed at 23°C. To the autoclave, 38 Nl of propylene was fed while rotating the stirring blade and ice cooling. Then, the autoclave was heated up to 80°C and pressurized with ethylene so that the total pressure would become 8 KG. When the internal pressure of the autoclave became 8 KG, 1.0 ml of a hexane solution of triisobutylaluminum (TIBA) (1.0 mM/ml) was forced into the autoclave with nitrogen. Subsequently, 3 ml of the previously prepared toluene solution containing 0.1 mM (in terms of Al) of methylaluminoxane and 0.001 mM of bis(1,3-dimethylcyclopentadienyl)zirconium dichloride was forced into the autoclave with nitrogen to initiate polymeri-zation. Thereafter, for a period of 60 minutes, temperature control of the autoclave was made so that the internal temperature would become 80°C, and ethylene was directly fed so that the pressure would become 8 KG. After 60 minutes from the initiation of polymerization, to the autoclave was fed 5 ml of methanol by means of a pump to terminate polymerization, and the pressure of the autoclave was released to atmospheric pressure. Then, 3 liters of methanol was poured into the reaction solution with stirring. The resulting polymer with the solvent was dried at 130°C and 600 Torr for 13 hours to obtain 34 g of an ethylene/propylene copolymer. Properties of the resulting polymer are set forth in Table 1.

Table 1

Properties of Ethylene/Propylene Copolymer				
Polymer properties	Polymerization Ex. 1	Polymerization Ex. 2	Polymerization Ex. 3	Polymerization Ex. 4
Ethylene content (wt%)	69.7	73.0	71.3	71.5
Mw (in terms of PS) $\times$ 10000	29.1	31.8	20.5	32.1

Table 1   (continued)

Properties of Ethylene/Propylene Copolymer				
Polymer properties	Polymerization Ex. 1	Polymerization Ex. 2	Polymerization Ex. 3	Polymerization Ex. 4
Mw/Mn	2.0	1.9	2.1	2.0
DSC-Tm (°C)	36.8	46.9	41.6	45.8
3.31×E-186	44.7	55.4	50.0	50.5
V (%)	1.5	1.4	1.5	1.8
10-0.1×E	3.0	2.7	3.0	2.9
I_{10}/I_2	9.4	9.8	8.2	6.3

Polymerization Example 5

[0126]   In a 2-liter continuous polymerization reactor equipped with a stirring blade, said reactor having been thoroughly purged with nitrogen, 1 liter of dehydrated and purified hexane was placed. To the reactor, a hexane solution of ethylaluminum sesquichloride ($Al(C_2H_5)_{1.5} \cdot Cl_{1.5}$) adjusted to a concentration of 8.0 mmol/l was continuously fed for 1 hour at a rate of 500 ml/hr. Then, to the reactor were further continuously fed a hexane solution of $VO(OC_2H_5)Cl_2$ (as a catalyst) adjusted to a concentration of 0.8 mmol/l at a rate of 500 ml/hr and hexane at a rate of 500 ml/hr. On the other hand, the polymer solution was continuously drawn out from the top of the polymerization reactor so that the amount of the polymer solution in the reactor would be invariably 1 liter. To the reactor were then fed ethylene at a rate of 230 l/hr, propylene at a rate of 70 l/hr and hydrogen at a rate of 4 l/hr using a bubbling tube. The copolymerization reaction was carried out at 35°C by circulating a cooling medium through a jacket equipped outside the polymerization reactor.

[0127]   Through the reaction under the above conditions, a polymer solution containing an ethylene/propylene copolymer was obtained. The polymer solution was deashed by the use of hydrochloric acid and then introduced into a large amount of methanol to precipitate the ethylene/propylene copolymer, which was then vacuum dried at 130°C for 24 hours. Properties of the resulting polymer are set forth in Table 2.

Table 2

Polymerization Conditions and Properties of Copolymer	
	Polymerization Ex. 5
Polymerization conditions	
Ethylene (l/hr)	230
Propylene (l/hr)	70
Hydrogen (l/hr)	4
Polymer properties	
Ethylene content (wt%)	70.5
Mw (in terms of PS) × 10000	30.2
Mw/Mn	2.0
DSC-Tm (°C)	26.7
3.31×E-186	47.4
V (%)	7.3
10-0.1×E	2.9
I_{10}/I_2	6.1

Example 1

[0128]   A lubricating oil was prepared using 89.04 % by weight of a mixed oil of mineral oil 100 Neutral/mineral oil 150 Neutral (available from ESSO Co.) in a mixing ratio of 80/20 as a lubricating oil base, 0.46 % by weight of the polymer obtained in Polymerization Example 1 as a viscosity index improver (viscosity modifier), 0.5 % by weight of Aclube 133 (available from Sanyo Kasei Co.) as a pour point depressant and 10 % by weight of a detergent dispersant (available from Lubrizole Co.). The lubricating oil was evaluated on the lubricating oil performance and flowability at

low temperatures. The results are set forth in Table 3.

Examples 2 - 4. Comparative Example 1

5   [0129]   A lubricating oil was prepared in the same manner as in Example 1. except for using a mixed oil of mineral
oil 100 Neutral/mineral oil 150 Neutral (available from ESSO Co.) in a mixing ratio of 80/20 as a lubricating oil base
and any one of the polymers obtained in Polymerization Examples 2 to 5 as a viscosity index improver in amounts
shown in Table 3. The lubricating oil was evaluated on the lubricating oil performance and flowability at low tempera-
tures. The results are set forth in Table 3.

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Table 3

Composition and Properties of Lubricating Oil					
	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 1
Type of ethylene/propylene copolymer added	Polymerization Ex. 1	Polymerization Ex. 2	Polymerization Ex. 3	Polymerization Ex. 4	Polymerization Ex. 5
Composition (wt%)					
lubricating oil base	89.04	89.04	88.78	89.04	89.04
detergent dispersant	10.0	10.0	10.0	10.0	10.0
copolymer	0.5	0.5	0.5	0.5	0.5
pour point depressant	0.46	0.46	0.72	0.46	0.46
Lubricating oil performance					
K.V. at 100°C (mm²/s)	10.08	10.16	10.15	10.10	10.05
SSI	49.0	48.0	32.0	47.0	46.0
CCS	2880	2780	2960	2820	2820
MRV	28500	23200	46000	24200	44500
low-temperature storage stability	AA	AA	AA	AA	AA
HTHS	3.25	3.24	3.28	3.20	3.06

Polymerization Example 6

Synthesis of olefin copolymer

[0130] In a 2-liter autoclave (made of SUS) equipped with a stirring blade, said autoclave having been thoroughly purged with nitrogen, 900 ml of heptane was placed at 23°C. To the autoclave, 13 Nl of propylene and 100 ml of hydrogen were fed while rotating the stirring blade and ice cooling. Then, the autoclave was heated up to 70°C and pressurized with ethylene so that the total pressure would become 6 KG. When the internal pressure of the autoclave became 6 KG, 1.0 ml of a hexane solution of triisobutylaluminum (TIBA) (1.0 mM/ml) was forced into the autoclave with nitrogen. Subsequently, 3 ml of the previously prepared toluene solution containing 0.02 mM (in terms of B) of triphenylcarbenium(tetrakispentafluorophenyl)borate and 0.0005 mM of (dimethyl(t-butylamido)(tetramethyl-η^5-cyclopentadienyl)silane)titanium dichloride was forced into the autoclave with nitrogen to initiate polymerization. Thereafter, for a period of 5 minutes, temperature control of the autoclave was made so that the internal temperature would become 70°C, and ethylene was directly fed so that the pressure would become 6 KG. After 5 minutes from the initiation of polymerization, to the autoclave was fed 5 ml of methanol by means of a pump to terminate polymerization, and the pressure of the autoclave was released to atmospheric pressure. Then, 3 liters of methanol was poured into the reaction solution with stirring. The resulting polymer with the solvent was dried at 130°C and 600 Torr for 13 hours to obtain 31 g of an ethylene/propylene copolymer. Properties of the resulting polymer are set forth in Table 4.

Polymerization Example 7

[0131] In a 2-liter autoclave (made of SUS) equipped with a stirring blade, said autoclave having been thoroughly purged with nitrogen, 900 ml of heptane was placed at 23°C. To the autoclave, 50 Nl of propylene was fed while rotating the stirring blade and ice cooling. Then, the autoclave was heated up to 60°C and pressurized with ethylene so that the total pressure would become 8 KG. When the internal pressure of the autoclave became 8 KG, 1.0 ml of a hexane solution of triisobutylaluminum (TIBA) (1.0 mM/ml) was forced into the autoclave with nitrogen. Subsequently, 3 ml of the previously prepared toluene solution containing 0.2 mM (in terms of Al) of methylaluminoxane and 0.002 mM of bis(1,3-dimethylcyclopentadienyl)zirconium dichloride was forced into the autoclave with nitrogen to initiate polymerization. Thereafter, for a period of 60 minutes, temperature control of the autoclave was made so that the internal temperature would become 60°C, and ethylene was directly fed so that the pressure would become 8 KG. After 60 minutes from the initiation of polymerization, to the autoclave was fed 5 ml of methanol by means of a pump to terminate polymerization, and the pressure of the autoclave was released to atmospheric pressure. Then, 3 liters of methanol was poured into the reaction solution with stirring. The resulting polymer with the solvent was dried at 130°C and 600 Torr for 13 hours to obtain 34 g of an ethylene/propylene copolymer. Properties of the resulting polymer are set forth in Table 4.

Polymerization Example 8

[0132] In a 2-liter continuous polymerization reactor equipped with a stirring blade, said reactor having been thoroughly purged with nitrogen, 1 liter of dehydrated and purified hexane was placed. To the reactor, a hexane solution of ethylaluminum sesquichloride (Al$(C_2H_5)_{1.5}$·Cl$_{1.5}$) adjusted to a concentration of 8.0 mmol/l was continuously fed for 1 hour at a rate of 500 ml/hr. Then, to the reactor were further continuously fed a hexane solution of VO(OC$_2$H$_5$)Cl$_2$ (as a catalyst) adjusted to a concentration of 0.8 mmol/l at a rate of 500 ml/hr and hexane at a rate of 500 ml/hr. On the other hand, the polymer solution was continuously drawn out from the top of the polymerization reactor so that the amount of the polymer solution in the reactor would be invariably 1 liter. To the reactor were then fed ethylene at a rate of 180 l/hr and propylene at a rate of 120 l/hr using a bubbling tube. The copolymerization reaction was carried out at 35°C by circulating a cooling medium through a jacket equipped outside the polymerization reactor.

[0133] Through the reaction under the above conditions, a polymer solution containing an ethylene/propylene copolymer was obtained. The polymer solution was deashed by the use of hydrochloric acid and then introduced into a large amount of methanol to precipitate the ethylene/propylene copolymer, which was then vacuum dried at 130°C for 24 hours. Properties of the resulting polymer are set forth in Table 4.

Table 4

Properties of Ethylene/Propylene Copolymer			
	Polymerization Ex. 6	Polymerization Ex. 7	Polymerization Ex. 8
Polymer properties			
Ethylene content (wt%)	47.2	46.8	49.6
Mw (in terms of PS) × 10000	19.6	20.1	19.2
Mw/Mn	2.1	2.0	1.8
DSC-Tm (°C)	-38.5	-36.2	-40.8
3.31×E-186	-29.8	-31.1	-21.8
V (%)	2.3	3.2	15.9
10-0.1×E	5.3	5.2	5.0
I_{10}/I_2	7.2	6.0	6.2

Example 5

[0134] A lubricating oil was prepared using 88.78 % by weight of a mixed oil of mineral oil 100 Neutral/mineral oil 150 Neutral (available from ESSO Co.) in a mixing ratio of 80/20 as a lubricating oil base, 0.72 % by weight of the polymer obtained in Polymerization Example 6 as a viscosity index improver, 0.5 % by weight of Aclube 133 (available from Sanyo Kasei Co.) as a pour point depressant and 10 % by weight of a detergent dispersant (available from Lubrizole Co.). The lubricating oil was evaluated on the lubricating oil performance and flowability at low temperatures. The results are set forth in Table 5.

Example 6, Comparative Example 2

[0135] A lubricating oil was prepared in the same manner as in Example 5, except for using a mixed oil of mineral oil 100 Neutral/mineral oil 150 Neutral (available from ESSO. Co.) in a mixing ratio of 80/20 as a lubricating oil base and the polymer obtained in Polymerization Example 7 or 8 as a viscosity index improver in amounts shown in Table 5. The lubricating oil was evaluated on the lubricating oil performance and flowability at low temperatures. The results are set forth in Table 5.

Table 5

Composition and Properties of Lubricating Oil			
	Ex. 5	Ex. 6	Comp. Ex. 2
Type of ethylene/propylene copolymer added	Polymerization Ex. 6	Polymerization Ex. 7	Polymerization Ex. 8
Composition (wt%)			
lubricating oil base	88.78	88.77	88.78
detergent dispersant	10.0	10.0	10.0
pour point depressant	0.5	0.5	0.5
copolymer	0.72	0.73	0.72
Lubricating oil performance			
K.V. at 100°C (mm²/s)	10.20	10.24	10.22
SSI	34.0	34.0	33.0
CCS	3240	3200	3300
MRV	41000	40000	48000
low-temperature flowability	AA	AA	AA
HTHS	3.28	3.24	3.08

Polymerization Example 9

Synthesis of olefin copolymer

[0136]　In a 2-liter autoclave (made of SUS) equipped with a stirring blade. said autoclave having been thoroughly purged with nitrogen, 900 ml of heptane was placed at 23°C. To the autoclave, 5 Nl of propylene and 90 ml of hydrogen were fed while rotating the stirring blade and ice cooling. Then, the autoclave was heated up to 70°C and pressurized with ethylene so that the total pressure would become 6 KG. When the internal pressure of the autoclave became 6 KG, 1.0 ml of a hexane solution of triisobutylaluminum (TIBA) (1.0 mM/ml) was forced into the autoclave with nitrogen. Subsequently, 3 ml of the previously prepared toluene solution containing 0.01 mM (in terms of Al) of methylaluminox-ane and 0.0004 mM of (dimethyl(t-butylamido)(tetramethyl-η^5-cyclopentadienyl)silane)titanium dichloride was forced into the autoclave wi⁺⁺ ⁻itrogen to initiate polymerization. Thereafter, for a period of 5 minutes, temperature control of the autoclave was m⸰ ⸳e so that the internal temperature would become 70°C, and ethylene was directly fed so that the pressure would become 6 kg. After 5 minutes from the initiation of polymerization, to the autoclave was fed 5 ml of methanol by means of a pump to terminate polymerization, and the pressure of the autoclave was released to atmospheric pressure. Then, 3 liters of methanol was poured into the reaction solution with stirring. The resulting polymer with the solvent was dried at 130°C and 600 Torr for 13 hours to obtain 35 g of an ethylene/propylene copolymer. Properties of the resulting polymer are set forth in Table 6.

Polymerization Example 10

[0137]　In a 2-liter autoclave (made of SUS) equipped with a stirring blade, said autoclave having been thoroughly purged with nitrogen, 900 ml of heptane was placed at 23°C. To the autoclave, 6 Nl of propylene and 120 ml of hydrogen were fed while rotating the stirring blade and ice cooling. Then, the autoclave was heated up to 40°C and pressurized with ethylene so that the total pressure. would become 6 KG. When the internal pressure of the autoclave became 6 KG, 1.0 ml of a hexane solution of triisobutylaluminum (TIBA) (1.0 mM/ml) was forced into the autoclave with nitrogen. Subsequently, 3 ml of the previously prepared toluene solution containing 0.016 mM (in terms of B) of triphenylcarbe-nium(tetrakispentafluorophenyl)borate and 0.0004 mM of (dimethyl(t-butylamido)(tetramethyl-η^5-cyclopentadienyl)si-lane)titanium dichloride was forced into the autoclave with nitrogen to initiate polymerization. Thereafter, for a period of 5 minutes, temperature control of the autoclave was made so that the internal temperature would become 40°C, and ethylene was directly fed so that the pressure would become 6 KG. After 5 minutes from the initiation of polymer-ization, to the autoclave was fed 5 ml of methanol by means of a pump to terminate polymerization, and the pressure of the autoclave was released to atmospheric pressure. Then, 3 liters of methanol was poured into the reaction solution with stirring. The resulting polymer with the solvent was dried at 130°C and 600 Torr for 13 hours to obtain 18 g of an ethylene/propylene copolymer. Properties of the resulting polymer are set forth in Table 6.

Table 6

Properties of Ethylene/Propylene Copolymer		
	Polymerization Ex. 9	Polymerization Ex. 10
Polymer properties		
Ethylene content (wt%)	70.5	70.8
Mw (in terms of PS) x 10000	29.5	31.9
Mw/Mn	2.0	1.8
DSC-Tm (°C)	44.5	39.0
3.31×E-186	47.4	58.3
V (%)	1.5	1.4
10-0.1×E	3.0	2.7
I_{10}/I_2	9.4	6.8

Example 7, Example 8

[0138]　A lubricating oil was prepared using a mixed oil of mineral oil 100 Neutral/mineral oil 150 Neutral (available from ESSO Co.) in a mixing ratio of 80/20 as a lubricating oil base, 0.46 % by weight of the polymer obtained in Polymerization Example 9 or 10 as a viscosity index improver, 0.5 % by weight of Aclube 133 (available from Sanyo Kasei Co.) as a pour point depressant and 10 % by weight of a detergent dispersant (available from Lubrizole Co.).

The lubricating oil was evaluated on the lubricating oil performance and flowability at low temperatures. The results are set forth in Table 7.

Table 7

Composition and Properties of Lubricating Oil		
	Ex. 7	Ex. 8
Type of ethylene/propylene copolymer added	Polymerization Ex. 9	Polymerization Ex. 10
Composition (wt%)		
lubricating oil base	89.04	89.04
Detergent dispersant	10.0	10.0
Pour point depressant	0.5	0.5
Copolymer	0.46	0.46
Lubricating oil performance		
K.V. at 100°C (mm²/s)	10.10	10.16
SSI	49.0	46.0
CCS	2910	2720
MRV	31500	22500
Low-temperature flowability	AA	AA
HTHS	3.25	3.20

Claims

1. A viscosity modifier for lubricating oil, comprising an ethylene/α-olefin copolymer which is a copolymer of ethylene and an α-olefin of 3 to 20 carbon atoms and has the following properties:

   (1) the ethylene content (E) is in the range of 40 to 77 % by weight,
   (2) the weight-average molecular weight (Mw) in terms of polystyrene, as measured by GPC, is in the range of 80,000 to 400,000,
   (3) Mw/Mn is not more than 2.4,
   (4) the melting point (Tm), as measured by DSC, is not higher than 60°C,
   (5) the ethylene content (E, % by weight) and the melting point (Tm, °C), as measured by DSC, satisfy the following relation (I):

$$3.31 \times E\text{-}186 \geq Tm \qquad (I),$$

   and
   (6) the proportion (V, %) of $\alpha\beta$ carbon atoms to all carbon atoms in the main chain, and if present, the long-chain branches, and the ethylene content (E, % by weight) satisfy the following relation (II):

$$V \leq 10\text{-}0.1 \times E \qquad (II).$$

2. The viscosity modifier for lubricating oil as claimed in claim 1, wherein the ethylene/α-olefin copolymer is an ethylene/propylene copolymer.

3. A lubricating oil composition comprising:

   (A) a lubricating oil base, and
   (B) an ethylene/α-olefin copolymer which is a copolymer of ethylene and an α-olefin of 3 to 20 carbon atoms and has the following properties:

   (1) the ethylene content (E) is in the range of 40 to 77 % by weight,

(2) the weight-average molecular weight (Mw) in terms of polystyrene. as measured by GPC. is in the range of 80.000 to 400,000.

(3) Mw/Mn is not more than 2.4,

(4) the melting point (Tm). as measured by DSC, is not higher than 60°C,

(5) the ethylene content (E, % by weight) and the melting point (Tm, °C) as measured by DSC satisfy the following relation (I):

$$3.31 \times E\text{-}186 \geq Tm \tag{I},$$

and

(6) the proportion (V, %) of $\alpha\beta$ carbon atoms to all carbon atoms in the main chain, and if present, the long-chain branches, and the ethylene content (E, % by weight) satisfy the following relation (II):

$$V \leq 10\text{-}0.1 \times E \tag{II};$$

wherein the ethylene/α-olefin polymer (B) is contained in an amount of 1 to 20 % by weight.

4. A lubricating oil composition comprising the lubricating oil base (A), the ethylene/α-olefin copolymer (B) and a pour point depressant (C), wherein:

the ethylene/α-olefin copolymer (B) is contained in an amount of 0.1 to 5 % by weight, and
the pour point depressant (C) is contained in an amount of 0.05 to 5 % by weight.

5. The lubricating oil composition as claimed in claim 3 or 4, wherein the ethylene/α-olefin copolymer (B) is an ethylene/α-olefin copolymer (B-1) having the following properties:

(1) the ethylene content (E) is in the range of 65 to 77 % by weight,

(2) the weight-average molecular weight (Mw) in terms of polystyrene, as measured by GPC, is in the range of 80,000 to 400,000,

(3) Mw/Mn is not more than 2.4,

(4) the melting point (Tm), as measured by DSC, is in the range of 15 to 60°C,

(5) the ethylene content (E, % by weight) and the melting point (Tm, °C), as measured by DSC, satisfy the following relation (I):

$$3.31 \times E\text{-}186 \geq Tm \tag{I},$$

and

(6) the proportion (V, %) of $\alpha\beta$ carbon atoms to all carbon atoms in the main chain, and if present, the long-chain branches, and the ethylene content (E, % by weight) satisfy the following relation (II):

$$V \leq 10\text{-}0.1 \times E \tag{II}.$$

6. The lubricating oil composition as claimed in claim 3 or 4, wherein the ethylene/α-olefin copolymer (B) is an ethylene/α-olefin copolymer (B-2) having the following properties:

(1) the ethylene content (E) is in the range of 40 to 55 % by weight,

(2) the weight-average molecular weight (Mw) in terms of polystyrene, as measured by GPC, is in the range of 80,000 to 400,000,

(3) Mw/Mn is not more than 2.4,

(4) the melting point (Tm), as measured by DSC, is not higher than -20°C,

(5) the ethylene content (E, % by weight) and the melting point (Tm, °C), as measured by DSC, satisfy the following relation (I):

$$3.31 \times E\text{-}186 \geq Tm \qquad\qquad (I).$$

and

(6) the proportion (V, %) of $\alpha\beta$ carbon atoms to all carbon atoms in the main chain, and if present. the long-chain branches, and the ethylene content (E, % by weight) satisfy the following relation (II):

$$V \leq 10\text{-}0.1 \times E \qquad\qquad (II).$$

7. The lubricating oil composition as claimed in any one of claims 3 to 6, wherein the ethylene/α-olefin copolymer (B) is an ethylene/propylene copolymer.

8. The lubricating oil composition as claimed in any one of claims 3 to 7, wherein the ethylene/α-olefin copolymer (B) is a copolymer having a ratio (I_{10}/I_2) of the melt index (I_{10}) as measured at 190°C under a load of 10 kg to the melt index (I_2) as measured at 190°C under a load of 2.16 kg ranging from 8 to 16.

9. The lubricating oil composition as claimed in any one of claims 3 to 7, wherein the ethylene/α-olefin copolymer (B) is a copolymer having a ratio (I_{10}/I_2) of the melt index (I_{10}) as measured at 190°C under a load of 10 kg to the melt index (I_2) as measured at 190°C under a load of 2.16 kg being not less than 5 and less than 8.

INTERNATIONAL SEARCH REPORT

	International application No.
	PCT/JP00/01902

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C10M143/00,
// C10N30:02, C10N30:08, C10N40:25, C08F210/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^7 C10M101/00-C10M177/00, C10N10:00-C10N80:00,
C08F4/60-C08F4/70, C08F6/00-C08F246/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI (DIALOG)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 3-131612, A (Idemitsu Kosan Co., Ltd.), 05 June, 1991 (05.06.91), Claims; page 2, upper left column, lines 4 to 11; page 4, upper right column, lines 5 to 12 (Family: none)	1-9
Y	EP, 420436, A1 (EXXON CHEMICAL PATENTS INC.), 03 April, 1991 (03.04.91), Claims; page 3, lines 10 to 14; page 8, line 40 to page 9, line 51; page 22, example 33, Table 2 & WO, 91/04257, A1 & JP, 3-188092, A & US, 5055438, A	1-9
Y	EP, 887355, A (Sumitomo Chemical Company, Limited), 30 December, 1998 (30.12.98), Claims; Column 2, line 1 to Column 10, line 31; Example 2 & JP, 11-71410, A & WO, 98/28341, A1	1-9
A	JP, 6-192327, A (Mitsui Toatsu Chemicals Inc.), 12 July, 1994 (12.07.94), the whole document (Family: none)	1-9

☒ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search	Date of mailing of the international search report
20 June, 2000 (20.06.00)	04 July, 2000 (04.07.00)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
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INTERNATIONAL SEARCH REPORT

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 5-148317, A (Mitsui Petrochemical Ind. Ltd.), 15 June, 1993 (15.06.93), the whole document (Family: none)	1-9
A	JP, 63-309592, A (Idemitsu Kosan Co., Ltd.), 16 December, 1988 (16.12.88), the whole document (Family: none)	1-9

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Non-Patent Literature

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_____ SPEC _____
Specification

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_____ TRNA _____
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_____ XT/ _____
Extension of Time filed separate

File Wrapper

_____ FWCLM _____
File Wrapper Claim

_____ IIFW _____
File Wrapper Issue Information

_____ SRFW _____
File Wrapper Search Info

Internal

_____ SRNT _____
Examiner Search Notes

_____ CLMPTO _____
PTO Prepared Complete Claim Set

_____ ECBOX _____
Evidence Copy Box Identification

_____ WCLM _____
Claim Worksheet

_____ WFEE _____
Fee Worksheet

REV 7/02/03

A Review of High Resolution Liquid 13Carbon Nuclear Magnetic Resonance Characterizations of Ethylene-Based Polymers

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I. INTRODUCTION

The use of ^{13}carbon nuclear magnetic resonance (NMR) spectroscopy in the molecular characterization of macromolecules has advanced our knowledge into structural areas that have been nearly impossible to measure by other spectroscopic techniques. Innovative applications have led to determinations of polymer configurational distributions, conomomer sequence distributions, average sequence lengths, structure and distribution of short chain branches, and analyses of nonreactive end groups. As a result, the importance of ^{13}C NMR to the field of polymer science cannot be overemphasized. The key to the success of ^{13}C-NMR studies in defining polymer molecular structure has been a structural sensitivity which encompasses more than just a few functional groups or carbon atoms. A sensitivity to polymer repeat unit sequences of lengths from two to as many as five, seven, and even nine contiguous repeat units [1, 2] has been observed. Of course, any structural technique that senses a unique response from as few as two successive repeat units will lead to a measurement of average sequence lengths [1, 3] and run numbers [4]. In addition to this excellent structural sensitivity, there has been an enormous improvement in the quantitative sensitivity of ^{13}C NMR in recent years. Detection of long-chain branching in polyethylene can now be made at a level of one per ten thousand carbon atoms [5], and newer generations of high field, higher sensitivity NMR spectrometers promise to extend this detection limit another order of magnitude.

It would be instructive at this point in this discussion to review some of the attributes that have made ^{13}C NMR so amenable to polymer structural analyses. For the sake of brevity, it will be assumed that the reader is basically familiar with the phenomenological descriptions of both ^{1}H and ^{13}C NMR. (It is a primary objective of this article to discuss the framework through which ^{13}C-NMR spectral information is transferred to useful polymer structural information, consequently very little time will be spent in phenomenological descriptions that are not required for an understanding of this "transfer process.") A significant advantage of ^{13}C NMR over corresponding NMR studies of other nuclei is that the ^{13}C nucleus has a spin of 1/2 and occurs at a natural abundance of approximately 1%. This latter property precludes any appreciable complications

from ^{13}C internuclear interactions and the former ensures isotropic magnetic behavior. Thus, from a quantum mechanical standpoint, ^{13}C NMR can be treated in a similar way to ^{1}H NMR. The carbon NMR spectral response to polymer structure is so sensitive to small changes that higher levels of ^{13}C isotopes would lead to hopelessly complex NMR spectral patterns, as encountered historically in corresponding ^{1}H-NMR studies of various homopolymers and copolymers [2]. Some isotopic ^{13}C labeling has been useful in certain polymers studies [6, 7];

however, the strength of the ^{13}C-NMR technique arises from the fact that ^{13}C nuclei are located in a sea of magnetically inactive ^{12}C nuclei and protons. The latter, although magnetically active, can be broad band noise decoupled cleanly and efficiently to remove all ^{13}C, ^{1}H interactions. The resulting spectra contain only single lines, each of which can be related to a specific carbon structural environment.

This part of the discussion leads us to the second major advantage of ^{13}C NMR of polymers, which is the wide range covered by ^{13}C chemical shifts. Expressed in ppm, the chemical shift is field independent and is defined by the frequency difference in hertz between an observed resonance and that of an internal standard divided by the ^{13}C-NMR resonance frequency (in MHz) as specified by the operating magnetic field. Typically, ^{13}C NMR covers a chemical shift range of over 200 ppm, which

is 20 times that usually encountered in ^{1}H NMR. In polymer spectra, this characteristic leads to well-delineated responses from the structural building units making up a polymer molecule.

The internal standard most often used in high-temperature NMR studies of polymers in solution is hexamethyldisiloxane (HMDS). Tetramethylsilane (TMS) is still the NMR chemical shift standard of choice but its low boiling point frequently precludes its use in NMR studies of polymers. It is preferable to report all polymer chemical shifts with respect to tetramethylsilane (TMS) by correcting the HMDS chemical shifts to a TMS standard. The chemical shift difference between TMS and HMDS is approximately 2.0 ppm, but the precise difference should be established independently on each spectrometer.

The final attributes contributing to the success of ^{13}C-NMR polymer structural analyses are a result of significant advances

in instrument technology. Operation in the Fourier transform mode [8] has made high sensitivities possible and permits a trade-off between high sensitivity and resolution [8] whenever desirable. Sometimes the low natural abundance of the ^{13}C isotope is easily glossed over in view of the ease with which ^{13}C-NMR spectra are obtained on the commercial NMR instrumentation available today. Broad-band decoupling [9] not only removes all ^{1}H spin-spin coupling with ^{13}C nuclei but also results in the creation of the nuclear Overhauser effect (NOE), a phenomenon that occurs only during broad-band decoupling and leads to enhancements in resonance intensities independently of the population of contributing nuclei. The magnitude of the nuclear Overhauser effect can be variable and is related to the specific mechanisms through which nuclear spins relax after excitement by a radiofrequency field. Fortunately for most polymers, the nuclear Overhauser effect is more an asset than a liability because of the restricted mobility of polymers [9], which leads to the dipole-dipole relaxation mechanism as the principal, if not the only, mode of nuclear relaxation. The nuclear Overhauser effect operates exclusively through the dipole-dipole relaxation mechanism, consequently most polymers exhibit the maximum NOE effect of 3.0 [9] and desirable quantitative analyses go unimpeded. If there is any question of differences among NOE's in polymer NMR spectra, gated decoupling experiments can be performed to ensure equal NOE's throughout the NMR spectrum [8]. These factors, together with a patient accumulation of data through time averaging, have led to quantitative measurements of concentration levels of one carbon type per 10,000 total carbon atoms, as mentioned earlier. It is this combination of good spectral sensitivity to low concentration levels in conjunction with excellent structural sensitivities that has made ^{13}C NMR so valuable in polymer characterization.

With the advantages of ^{13}C NMR now briefly reviewed, it is appropriate at this point to discuss polymer structure in terms of a framework compatible with the information retrieved from ^{13}C-NMR analyses. "Polymer structure" can evoke a different response, depending upon the particular area of interest, from various polymer scientists. It can encompass morphological structures, properties, molecular weights, and even flow properties of polymer melts. Polymer structure in this discussion will refer to the actual molecular chain structure, that is, the identity of the repeat unit and its chirality, sequence structures and their distributions, the identity of end

groups including numbers and types per molecule, the degree of polymerization, and the identification of both short- and long-chain branching. For homopolymers, the interest in polymer molecular structure is limited to the degree of polymerization, chirality and variation in modes of monomer additions, the identity of end groups, and extent of long-chain branching. Copolymer structural analyses encompass all of the factors encountered in analyses of homopolymers but with additional complications arising from various possible sequence distributions. Homopolymers with one pendant group per repeat unit can often be treated as copolymers because of chiral differences that may arise within repeat unit sequences. Mathematically, sequence distributions are treated in the same way whether they arise from chiral differences or differences in repeat unit structures created by using different comonomers during polymerization. Because polymer chirality is inherently included in A,B copolymer descriptions and has been well covered independently previously [2, 3], the development of structural concepts and characterization parameters in the upcoming discussion will be limited to A,B types of copolymers. The mathematical treatment is, therefore, quite general but will be applied exclusively to ethylene-based polymers, that is, low-density polyethylene, linear low-density polyethylenes, and ethylene-vinyl acetate copolymers, which are also produced free radically in a high-pressure process.

Prior to the advent of ^{13}C NMR, knowledge of repeat unit structure and the relative A,B concentrations for copolymers was usually all that could be determined from a micromolecular structural viewpoint. Endgroup concentrations could be measured for many step-growth polymers if the polymer chain ended in a functional group that was active chemically, but aliphatic end groups from chain-growth polymers usually went uncharacterized. Repeat unit structures of both chain-growth and step-growth polymers were often determined by either infrared or ^{1}H NMR. The missing ingredient in most copolymer analyses was the concentration of unlike contiguous pairs of polymer repeat units, that is, the AB+BA diad concentration. Any polymer chain, whether a homopolymer or copolymer, can be visualized as being derived from any one or all of the three exclusive types of diads, that is, AA, AB+BA, or BB. Knowledge of the three diad concentrations, whether absolute or relative, leads to the A,B mole fractions, average sequence lengths for both A and B, and the "run number," which is the number of runs collectively of both units per 100 contiguous repeat units, as defined by Harwood and Ritchey [4]. The